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Aliphatic Esters of the 9,10-Dihydroxystearic Acids

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Although the 9,10-dihydroxystearic acids, m. p. 95 and 130°, derivable from oleic and elaidic acids, are well-known compounds, a search of the literature revealed that only their methyl and ethyl esters had been reported.[2] Interest in plasticizers and high-melting waxes prompted us to prepare a series of esters of these hydroxy acids with aliphatic primary alcohols ranging in chain length from three to eighteen carbon atoms. The results are summarized in Tables I and II. The esters are white, crystalline solids, with very low vapor pressures. They are insoluble in water but are soluble in most organic solvents. It is interesting to note that in the series of low-melting esters, the *n*-butyl ester has the minimum melting point, whereas in the series of high-melting esters, the *n*-amyl ester has the minimum melting point.

Experimental

Materials.—The 9,10-dihydroxystearic acids, m. p. 95 and 130°, were prepared from oleic acid by oxidation with hydrogen peroxide in acetic acid solution[3] and with alkaline potassium permanganate,[4] respectively. The 9,10-dihydroxyoctadecyl alcohol, m. p. 84.5–86°, was prepared from oleyl alcohol.[5] The other alcohols were Eastman Kodak Company purest grade, and they were either crystallized to constant melting points or fractionally distilled before use.

TABLE I

PROPERTIES OF ESTERS OF 9,10-DIHYDROXYSTEARIC ACID, M. P. 130°

Ester[a]	Yield,[b] %	M. p., °C.	Saponification no. Calcd.	Saponification no. Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
n-Propyl	51	92.5–93.5	156.4	156.0	70.4	70.2	11.8	11.5
n-Butyl	50	89–90	150.6	150.5	71.0	71.2	11.9	11.5
i-Butyl	18	89.5–90.5	150.6	150.3	71.0	71.0	11.9	11.6
n-Amyl	46	86.5–88	145.1	145.6	71.4	71.5	12.0	11.5
n-Hexyl	55	87–87.5	140.0	140.3	72.0	72.0	12.1	12.1
n-Octyl	54	88–89	130.9	131.6	72.9	73.0	12.2	11.6
n-Decyl	52	89.5–90.5	122.8	124.1	73.6	74.0	12.4	11.9
n-Dodecyl	59	91–92	115.7	116.0	74.3	73.9	12.5	12.0
n-Tetradecyl	65	92–93	109.4	109.7	75.0	74.8	12.6	12.0
n-Hexadecyl	69	94–95.5	103.7	104.4	75.5	75.5	12.7	12.5
n-Octadecyl	64	94–95	98.7	99.7	76.0	75.9	12.8	12.5
9,10-Dihydroxyoctadecyl	56	107–108.5	93.4	92.1	71.9	71.6	12.1	11.8

[a] The methyl ester, m. p. 105°, and the ethyl ester, m. p. 99°, have been reported in the literature.[2] [b] Purified products.

TABLE II

PROPERTIES OF ESTERS OF 9,10-DIHYDROXYSTEARIC ACID, M. P. 95°

Ester[a]	Yield,[b] %	M. p., °C.	Saponification no. Calcd.	Saponification no. Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
n-Propyl	25	57.5–58	156.4	156.4	70.4	69.8	11.8	11.7
n-Butyl	51	53–54	150.6	150.3	71.0	70.9	11.9	11.7
n-Amyl	30	58.5–59.5	145.1	145.2	71.4	71.5	12.0	12.0
n-Hexyl	46	64.5–65.5	140.0	140.4	72.0	72.0	12.1	11.5
n-Octyl	55	73–74	130.9	130.8	72.9	72.5	12.2	12.3
n-Decyl	63	72.5–73	122.8	123.2	73.6	73.6	12.4	12.2
n-Dodecyl	40	70–72	115.7	115.8	74.3	74.5	12.5	12.1
n-Tetradecyl	50	71.5–72	109.4	110.6	75.0	74.4	12.6	11.6
n-Hexadecyl	55	73–74	103.7	105.0	75.5	75.4	12.7	12.5
n-Octadecyl	63	76–77	98.7	99.9	76.0	75.8	12.8	12.5
9,10-Dihydroxyoctadecyl	60	96.5–97.5	93.4	92.1	71.9	72.3	12.1	12.1

[a] The methyl ester, m. p. 71°, and the ethyl ester, m. p. 59°, have been reported in the literature.[2] [b] Purified products.

Esterification Procedures.—The propyl and butyl esters were prepared by heating 15.8 g. (0.05 mole) of 9,10-dihydroxystearic acid, 32 ml. of the alcohol, and 0.316 g. of naphthalene-β-sulfonic acid for eight hours at 100°. The solution was poured into a large excess of hot water (90°), with stirring and the lower aqueous layer was discarded.

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) Hilditch, *J. Chem. Soc.*, 1828 (1926); Smit, *Rec. trav. chim.*, **49**, 675 (1930). Ishikawa and Kuroda [*Science Repts. Tokyo Bunrika Daigaku*, **A3**, 265 (1939)] have prepared a series of aliphatic esters from the dihydroxystearic acid isolable from castor oil.

(3) Scanlan and Swern, THIS JOURNAL, **62**, 2305 (1940).

(4) Le Sueur, *J. Chem. Soc.*, **79**, 1313 (1901).

(5) Swern, Findley and Scanlan, THIS JOURNAL, **66**, 1925 (1944).

The crude ester was washed once with hot water. The dry crude ester, obtained in nearly quantitative yield, was recrystallized to a constant melting point from 95% ethanol (5 ml./g.).

The higher alcohol esters were prepared by refluxing 15.8 g. of 9,10-dihydroxystearic acid, 0.06 mole of the alcohol, 200 ml. of benzene, and 0.316 g. of naphthalene-β-sulfonic acid for eight hours. The water formed during the reaction was removed azeotropically, and the benzene was returned to the reaction mixture. The quantitative amount of water was liberated. The benzene solution was evaporated to dryness, and the crude ester was melted and washed once with hot water. The aqueous layer was discarded, and the dried product, obtained in quantitative yield, was recrystallized to a constant melting point from 95% ethanol (5 ml./g.)

Summary

The 9,10-dihydroxystearic acids, m. p. 95° and 130°, have been esterified with twelve saturated aliphatic primary alcohols. The products are fairly high melting solids with very low vapor pressures. They may be useful as plasticizers or high-melting waxes.